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Polymerizable Amine Mixtures, Amine Polymer Materials and their Use

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Field of Invention

The present invention relates to the use of at least one organic amine derivative, which is capable of forming a crosslinked polymer with itself and/or with at least one multifunctional compound, and/or its crosslinked polymer product obtainable by crosslinking said amine derivative with itself or with at least one multifunctional compound, for the manufacture of dielectric layers of electronic devices. Furthermore, the invention relates to a polymerizable amine mixture and an amine polymer material. In addition, the invention relates to a process for the manufacture of a dielectric layer of an electronic device and to such electronic devices.

Background and Prior Art

Organic electronic devices, like e.g. organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic integrated circuits, are currently the object of intense research. One major advantage are the lower production costs compared to the conventional silicon based electronic devices, especially when a high number of pieces and/or large areas with electronic and/or optical functionalities are involved. Further advantages arise from the mechanical flexibility and light-weight properties of such organic based devices.

So far, in the development of organic electronic devices, especially OFETs, much effort has focussed on optimisation of the semiconductor and conducting material properties. However as the charge flow in a working device occurs primarily at the semiconductor-insulator interface, a successful device does also require optimisation of the film and electrical behaviour of the insulator. Typical device structures are illustrated in the papers by C.J. Drury et al., Applied Physical Letters, 73, 1998, 108-110; Z. Bao, Advanced Materials, 12, 2000, 227-230; M. Matters et al., Optical Materials, 12 1999, 189-197; H. Sirringhaus et al., Applied Physical Letters, 77, 2000, 406-408; Z. Bao, J.A. Rogers and H.E. Katz, J. Mater.

Chem. 9, 1999, 1895-1904; Z. Bao, Y. Feng et al., Chem. Mater. 9, 1997, 1299-1301.

A promising approach for large scale, low cost manufacture of organic based integrated circuits is that fabrication steps are carried out by solution processing. This allows the possibility for roll-to-roll processing, where large areas can be coated and printed at high speed. Key requirement for an insulator compatible with this technique is a sufficient solubility in a process appropriate solvent to ensure that the solution wets and coats the surface, and that the film formed is coherent. This requires optimisation of the solution rheology and evaporation rates. In addition, for a multilayer structure, it is essential that the solvent used in deposition of each layer does not dissolve or swell the layer on which it is in contact with, thus preventing poor interfaces and interlayer diffusion. As each layer is applied via solution, then a solvent with an incompatible solubility parameter to the previous layer is required, sometimes referred to as an orthogonal solvent. This solvent parameter latitude can be significantly widened if the previous layer can undergo a chemical process such as crosslinking. By crosslinking the film in situ, shorter potentially mobile molecular units are tethered into an immobile network. Excessive crosslinking however, can cause excessive shrinkage and brittle films, therefore good control of the chemistry is required.

In a common device structure, the insulator is applied onto the semiconductor surface. Most semiconductors contain aliphatic chains, which impart solubility and often improve morphology. However, the consequence of this chemical structure is that the aliphatic groups are thermodynamically driven to the semiconductor surface, rendering it hydrophobic and of very low energy. This makes wetting the surface during solution application of the insulator an important consideration.

Working devices require an insulator which exhibits high electrical resistivity, has an optimum dielectric constant as defined by the geometry of the device, and is chemically inert during the lifetime of the device. High electronic bandgap organic materials provide excellent electrical insulation, whereas the dielectric constant of the film is a function of the electronic

polarizability, and is frequency dependant. The electronic polarizability can be increased by addition of polar groups.

Many current OFET devices utilise polyvinyl phenol (PVP) (see literature cited above) as the insulating layer, which can be crosslinked with hexamethoxymethylmelamine (a melamine formaldehyde resin) to reduce its solubility (C.J. Drury, cited above). This melamine derivative is employed as a simple crosslinker and does not possess acceptable solution rheology or film properties for large scale production, especially using roll-to-roll processing. However, PVP can be susceptible to oxidation, is acidic, hygroscopic, and PVP melamines require elevated temperatures to achieve crosslinking. As a result, the achieved reliability is not always sufficient, which involves extra steps adding to the processing costs.

Polymethylmethacrylate (PMMA) has also been utilised as an insulating layer (Z. Bao and Z. Bao, J.A. Rogers and H.E. Katz, both cited above). This polymer, however, cannot be crosslinked, and therefore will be susceptible to swelling and dissolution in the subsequent solution processing step. This leads to poor interfaces. In addition, as PMMA is a homopolymer with no reactive functionality, the chemical composition is fixed, and, unlike PVP, cannot be tailored to fine tune its properties unless an additional polymer is introduced as a blend. In addition, the dielectric constant of PMMA is relatively low.

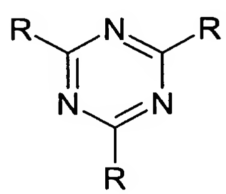
Another common choice of an insulator material is polyimide (PI) (Z. Bao; Z. Bao, J.A. Rogers and H.E. Katz; and Z. Bao, Y. Feng et al., all cited above). This material can be applied via solution as the polyacid amide precursor and thermally converted to polyimide, with the elimination of water. There are two significant disadvantages of this process, namely that it requires a high temperature for the dehydration step, and that water is formed, which can be difficult to remove from the device, and cause stability problems and higher off currents.

Furthermore, silicon dioxide is used as an insulator material. It requires high temperature deposition techniques which are not compatible with a

roll-to-roll fabrication process and does not have any mechanical flexibility and is therefore not suitable for flexible organic electronic devices.

A large number of different organic amine derivatives, which are capable of forming a crosslinked polymer with themselves and/or with at least one multifunctional compound, are known. Typical amine derivatives are amine resins, i.e. resins of amine derivatives and formaldehyde. Common amine precursors are melamine, urea or benzoguanamine and their derivatives.

US 4,312,988 describes the synthesis of melamine derivatives of the formula

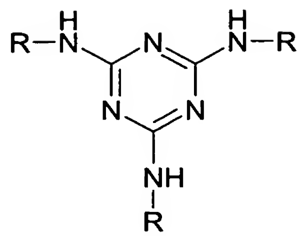


wherein each R is selected from alkyl, cycloalkyl, aryl, NH_2 and NHR.

In US 4,424,261 a composition comprising a blend of a hydroxyalkyl melamine or a reaction product of a hydroxyalkyl melamine and formaldehyde and a melamine formaldehyde resin is disclosed. Such compositions are used as the resin component of heat and pressure consolidated laminates.

US 4,578,312 discloses an insulating material comprising a phenoxy resin with a molecular weight higher than 10.000, cured with at least two materials, one of which can be an amine derivative resin among many others.

US 4,670,558 describes the preparation of amidoalkylmelamines and aminoalkylmelamines of the formula



wherein at least one R is an amidoalkyl group -$(CH_2)_n$-NHZ or an aminoalkyl group -$(CH_2)_n$-NH_2, n is from 2 to 10 and Z is an amino protective group.

US 4,886,882 discloses hydroxyoxaalkylmelamines of the above given formula, wherein the groups R may be identical or different and are each H or -(CHR'-CHR'-O-$)_n$-H, with R' is H or C_{1-4} alkyl and n is 2 or 3. These amine derivatives are useful for the preparation of urethanes or aminoplast resins.

The preparation of polyalkoxymethylmelamine is described in US 5,017,699. Melamine is reacted with formaldehyde, followed by alkylation with an excess of alcohol in the presence of a superacid catalyst.

Aims of the invention

It is an aim of this invention to provide amine derivatives and/or their crosslinked polymer products which fulfill, at least in part, the requirements of a dielectric material or its precursor, being processable from solution, and circumvents, at least in part, the disadvantages of known dielectric materials as described in the introduction.

Furthermore, it is an aim of this invention to provide amine derivatives and/or their crosslinked polymer products which show advantageous solution properties with respect to rheology and intercoat adhesion and are therefore especially suited for the manufacture of dielectric layers of electronic devices.

A further aim of this invention is to provide a polymerizable amine mixture which shows advantageous solution properties with respect to rheology and intercoat adhesion.

Therefore, an amine polymer material obtainable from such a mixture is an additional aim of the invention.

Furthermore, this invention has the aim to show a method for the manufacture of dielectric layers of electronic devices, which is especially suited for the production of a high number of pieces and/or large areas.

Additional aims of this invention concern organic electronic devices.

Other aims of the present invention are immediately evident to a person skilled in the art from the following detailed description.

Definition of Terms

The term electronic device encompasses all devices and components with electronic, preferably microelectronic, including electrooptical functionality, like e.g. resistors, diodes, transistors, integrated circuits, light emitting diodes and electrooptical displays. In particular, the term electronic device includes organic electronic devices, i.e. all electronic devices and components in which at least one functionality, like e.g. conduction, semiconduction and/or light emission, is realized by a polymer and/or an organic material. Examples of such organic electronic devices are organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and devices which contain a number of such components, like polymeric integrated circuits, e.g. containing OFETs, and active matrices, e.g. comprising thin film transistors (TFTs) of liquid crystal displays (LCDs) and other displays.

The term dielectric layer or material means a layer or material exhibiting very low or even non-conducting electrical properties, in particular with a resistivity greater or equal than 10^{+8} Ωcm.

The term layer as used in this application includes coatings on a supporting substrate or between two substrates, as well as self-supporting, i.e. free-standing, films that show more or less pronounced mechanical stability and flexibility. The layer may be flat or may be varyingly shaped in any of the three dimensions, including patterned.

The term substrate as used in this application relates to the part of the organic device that the amine mixture is coated onto.

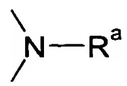
The term substrate is also used for the starting material used as a base for the device. This material is typically silicon wafer, glass or plastic (e.g. PET foil). In a typical transistor device the source and drain electrode will have already been structured onto the surface (lithography, thermal evaporation or printing methods). On top of this structure a surface energy modification layer or an alignment layer is optionally deposited, then the semiconductor (e.g. polyhexylthiophene), the insulator, i.e. the amine mixture, and finally the gate electrode is arranged.

Summary of the Invention

One of the objects of this invention is the use of at least one organic amine derivative, which is capable of forming a crosslinked polymer with itself and/or with at least one multifunctional compound, and/or its crosslinked polymer product obtainable by crosslinking said amine derivative with itself or with at least one multifunctional compound, for the manufacture of dielectric layers of electronic devices.

Preferred is the use of at least one organic amine derivative, which is capable of forming a crosslinked polymer with itself and/or with at least one multifunctional compound, and/or its crosslinked polymer product obtainable by crosslinking said amine derivative with itself or with at least one multifunctional compound, as the main component of a composition for the manufacture of dielectric layers of electronic devices.

In another preferred embodiment, the amine derivative comprises two or more identical or different groups of the subformula I



I

wherein

R^a	is H, $-[(CR'R'')_v-CO]_r-R'''$, $-[(CR'R'')_v-O-]_r-R'''$ or $-(CR'R'')_v-NHZ$,
R', R'', R'''	are independently of each other H, an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen,
Z	is H or a protective group,
v	is 0 or greater or equal to 1, and
r	is greater or equal to 1, wherein if v is 0, then r is 1.

A further object of this invention is a polymerizable amine mixture comprising

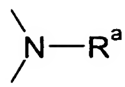
50 to 99.5 % by weight of component A,

0 to 50 % by weight, preferably 0.5 to 50 % by weight of component B, and

0 to 10 % by weight of component C,

wherein

A: is at least one organic amine derivative, which is capable of forming a crosslinked polymer with itself and/or with at least one multifunctional compound, wherein the amine derivative comprises two or more identical or different groups of the subformula I



I

wherein

R^a is H, $-[(CR'R'')_v-CO]_r-R'''$, $-[(CR'R'')_v-O-]_r-R'''$ or $-(CR'R'')_v-NHZ$,

R', R'', R''' are independently of each other H, an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen,

Z is H or a protective group,

v is 0 or greater or equal to 1,

r is greater or equal to 1, wherein if v is 0, then r is 1,

B: is at least one multifunctional compound, being capable of reacting with at least one component of A to form a crosslinked polymer, and

C: is at least one initiator for the polymerization of the component A or the components A and B.

Another object of the present invention is an amine polymer material obtainable by polymerization of a polymerizable amine mixture according to the invention.

A further object of this invention is a process for the manufacture of a dielectric layer of an electronic device comprising the steps

a) preparing a substrate which optionally comprises one or more layers or patterns of materials with insulating, semiconductive, conductive, electronic and/or photonic functionalities,

b) forming a thin layer of a polymerizable amine mixture comprising one or more amine derivatives as defined in the foregoing and in the following onto said substrate or onto defined regions of said substrate, and

c) initiating the polymerization of the polymerizable amine mixture of said thin layer.

An additional object of this invention refers to an electronic device obtainable by the process according to the present invention.

Furthermore, an object of this invention refers to an electronic device comprising an amine polymer material according to this invention as a dielectric.

Detailed Description of the Invention

It has been found that amine derivatives comprising groups of the subformula I show advantageous solution properties with respect to rheology and intercoat adhesion and are therefore especially suited for the manufacture of dielectric layers of electronic devices. This finding also holds for their crosslinked polymer products, obtainable by crosslinking said amine derivative with itself or with at least one multifunctional compound. In addition these derivatives can effectively wet a low energy hydrophobic surface, especially surfaces of organic semiconducting materials. Furthermore, it has been observed that by either self-crosslinking the amine derivative according to the invention or crosslinking it with at least one multifunctional compound advantageous changes in electric, viscoelastic behaviour and densification, i.e. improved flexibility, elasticity, durability, solvent resistance and/or insulator characteristics can be achieved.

The amine derivatives according to the present invention possess functional groups that are capable of undergoing chemical reactions either with themselves or a co-component, especially with a multifunctional compound as defined in the following, to form a crosslinked polymer

network. The chemical reaction is controllable, in that at least at room temperature, i.e. 20°C, or below the amine derivative can be stored with essentially no chemical reaction occuring. The chemical reaction can be initiated by, e.g. rising the temperature, altering the pH, exposing to electromagnetic or particle radiation or to reactive compounds.
Those amine derivatives are preferred, which, cross-linked with themselves or one or more multifunctional compounds, result in stable dielectric films of high resistivity, especially a resistivity greater or equal than 10^{+8} Ωcm.

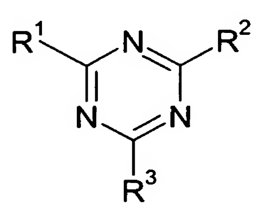
Preferably, the amine derivative according to the invention comprises two or more groups of the subformula I as defined above wherein at least one of the groups R^a comprises an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen.

Furthermore, the amine derivative according to the invention comprises preferably one or more -OH groups. Most preferably it comprises two or more groups of the subformula I as defined above wherein at least one of the groups

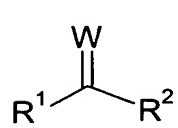
R^a is $-[(CR'R'')_v-O-]_r-H$

and R', R'', v and r are as defined above.

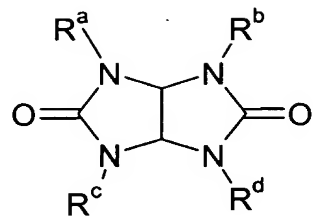
According to a preferred embodiment of the invention, the amine derivative is selected from the following group of formulae I.1 to I.3



I.1



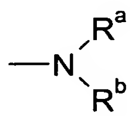
I.2



I.3

wherein

R^1, R^2, R^3 are independently of each other a group of formula II



II

R^a, R^b, R^c, R^d are independently of each other H, $-[(CR'R'')_v\text{-}CO]_r\text{-}R'''$, $-[(CR'R'')_v\text{-}O\text{-}]_r\text{-}R'''$ or $-(CR'R'')_v\text{-}NHZ$,

R', R'', R''' are independently of each other H, an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen,

Z is H or a protective group,

v is 0 or greater or equal to 1,

r is greater or equal to 1, wherein if v is 0, then r is 1,

W is O or S,

R^3 may, in addition to the foregoing meaning, be an alkyl, cycloalkyl, aryl or alkylaryl group, which is optionally substituted by halogen.

In the following the groups, substituents and indices R^1, R^2, R^3, R^a, R^b, R^c, R^d, R', R", R"', Z, v, r and n have the above given meaning unless stated otherwise.

It is emphasized that each group, substituent and index occuring twice or more in one of the foregoing or following formulae may have identical or different meanings.

By the choice of the substituents R^a and R^b, the physical and chemical properties of the amine derivative, of its polymerizable mixture and of the resulting polymer can be influenced in order to meet the requirements for the manufacture of dielectric layers of organic electronic devices. Furthermore, the processing of a polymerizable mixture comprising such an amine derivative and its polymerization characteristic is influenced by the substituents R^a and R^b.

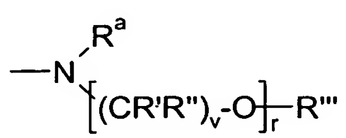
Those amine derivatives selected from the group of formulae I.1 to I.3 are preferred wherein at least one of the groups R^1, R^2, R^3 and/or of the groups R^a, R^b, R^c, R^d comprises an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen.

Z is H or a protective group of an amino function, like e.g. formyl, tosyl, acetyl, trifluoroacetyl, methoxy, ethoxy, tert.-butoxy, cyclopentyloxy as well as phenoxycarbonyl, carbobenzyloxy and p-nitrobenzyloxy.

The index v is preferably 1 to 6, most preferably 1 or 2.

The index r is preferably 1 to 4, most preferably 1 or 2.

Those derivatives selected from the group of formulae I.1 and I.2 are preferred, wherein one, two or three of the groups R^1, R^2, R^3 are a group of formula IIa



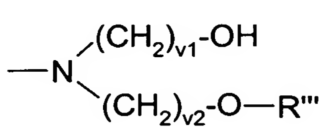
IIa

wherein R^a, R', R", R"', v and r have the meaning given above.

According to the preferred embodiment of formula IIa, the following variants themselves or the combination of two or more of these variants are preferred:

- two or three of the groups R^1, R^2, R^3 of formulae I.1 and I.2 have independently of each other the meaning according to formula IIa.
- R"' is an alkyl group with 2 to 12 C-atoms, preferably with 3 to 12 C-atoms, which may be substituted by halogen.
- R"' is an alkyl group with 2 to 8 C-atoms, preferably 3 to 8 C-atoms, most preferably with 3, 4, 5 or 6 C-atoms, wherein one, more or all H-atoms may be substituted by halogen, preferably by F or Cl.
- r is 1 or 2, preferably 1.
- v is 1, 2, 3 or 4, preferably 1.
- R' and R" are H.
- R^a is H or comprises at least one -OH group.
- R^a is $-[(CR'R")_v-O-]_r-H$, wherein R', R", v and r are as defined above, preferably R' and R" are H, v is preferably 1, 2, 3 or 4, most preferably 1 or 2 and r is preferably 1 or 2, most preferably 1.
- R^a is $-CH_2-OH$.

Furthermore those derivatives selected from the group of formulae I.1 and I.2 are preferred, wherein one, two or three of the groups R^1, R^2, R^3 are independently of each other a group of formula IIb



IIb

wherein

v1 is 0, 1, 2, 3 or 4, preferably 1,

v2 is 1, 2, 3 or 4, preferably 1,

R''' is preferably H or an alkyl group with 1 to 12 C-atoms, preferably 2 to 8 C-atoms, wherein one, more or all H-atoms may be substituted by halogen, preferably by F or Cl.

Beside the preferred condition, that at least one of the groups R^1, R^2, R^3 and/or of the groups R^a, R^b, R^c, R^d comprises an alkyl group with 1 to 12 C-atoms or an alkenyl group with 2 to 12 C-atoms, which may be substituted by halogen, it has been found, that

- if at least one of R^a, R^b is H, a fast cure response and a good film hardness is achieved.
- if at least one of R^a, R^b is -OH or $-CH_2OH$, a mixture comprising this amine derivative shows advantageous rheology properties.
- if at least one of R^a, R^b is $-(CH_2)_v$-O-R''', wherein $v \geq 1$ and R''' is an alkyl group, in particular with 2 or more C-atoms, a more flexible dielectric layer is obtainable.
- if at least one of R^a, R^b is $-(CH_2)_v$-CO-R''', wherein $v \geq 1$ and R''' is an alkyl group, in particular with 2 or more C-atoms, relatively low viscosities, improved flow, leveling and wetting properties and a good intercoat adhesion of a polymerizable mixture comprising the inventive amine derivative is obtainable. Furthermore, the mixture shows a high formulation stability and the resulting dielectric layer has a good flexibility.

The amine derivatives according to this invention may possess beside N-H, $N-CH_2-OH$ and/or $N-CH_2$-O-Alkyl functionalities also -CO- groups.

Therefore, amine derivatives, which exhibit not only one kind of substituent, but a combination of different substituents, especially those mentioned in the foregoing, and/or combinations of two or more amine derivatives according to the invention are preferred, in order to meet the requirements of the processing techniques for the manufacture of dielectric layers of organic electronic devices and the requirements of the dielectric layers themselves.

In the following, advantages, preferred embodiments and variants of the polymerizable amine mixture according to the invention are described.

Using the polymerizable amine mixture according to the invention, even hydrophobic surfaces, in particular with surface energies lower than 20 mN/cm, can be wetted and coated, yielding a coherent film, which can be cured. Thus, also patterns or layers of materials with low and very low surface energy, like, e.g. of semiconductive polymers with aliphatic chains to improve their solubility, can be coated with the inventive dielectric amine derivative material.

Those amine derivatives are preferred as component A which were described in the foregoing, especially an amine derivative or a combination of 2, 3 or more amine derivatives according to formula I.1 and/or I.2, wherein one, two or three of the substituents R^1, R^2, R^3 are independently of each other of formula II, in particular of formula IIa and/or IIb.

In a preferred embodiment, melamine-formaldehyde resins and urea-formaldehyde resins are used as component A. Commercially available melamine-formaldehyde resins using, e.g. the brandname ®Cymel are commercially available from CYTEC INDUSTRIES INC., West Paterson, NJ 07424, USA. A commercially available urea-formaldehyde resin is UI20-E from CYTEC INDUSTRIES INC., West Paterson, NJ 07424, USA.

Component B is at least one multifunctional compound, being capable of reacting with at least one component of A to form a crosslinked polymer. The multifunctional compound is advantageously chosen such that the resulting mixture exhibits good rheological properties with respect to the employed manufacture techniques of thin dielectric layers. Furthermore, the mechanical and electrical properties of the resulting dielectric layer can be influenced by the choice of the multifunctional compound. In addition, the water uptake of the resulting amine polymer can be minimised by employing multifunctional compounds with at least one hydrophobic group, like, e.g. aliphatic alkyl chains.

Preferably, at least one multifunctional compound of component B is an organic compound with at least two functional groups from the class consisting of -OH, $-NH_2$, -COOH and their reactive derivatives, being

capable of reacting with at least one component of A to form a crosslinked polymer. Preferred multifunctional compounds are aliphatic, cycloaliphatic and aromatic dioles, polyoles, diacids, polyacids, diamines, polyamines and their reactive derivatives. Reactive derivatives are advantageously such derivatives, from which the desired functional group can be set free under appropriate reaction conditions, like, e.g. by elimination of a protective group. Classes of preferred multifunctional compounds are alkanedioles with 2 to 12 C-atoms, polyhydroxyalkyl (meth)acrylates, poly (meth)acrylic acids, polyols and optionally substituted phenol formaldehyde condensation copolymers. Examples of such compounds are 1,4-butanediol, polyhydroxyethyl methacrylate, polyacrylic acid, polyurethane polyols, polyethylene imine, polyvinyl phenol as well as cresol formaldehyde condensation copolymer. A commercially available polyurethane polyol is K-Flex diol DU 320 from KING INDUSTRIES (2741 EZ Waddinxveen, The Netherlands). A commercially available cresol formaldehyde condensation copolymer is Novolak AZ 520D from Clariant GmbH, 65926 Frankfurt am Main, Germany.

Component C is at least one initiator for the polymerization of the component A or the components A and B. Suitable initiators are acids or bases and compounds which set free an acid or a base under appropriate reaction conditions, like, e.g. by heat or actinic radiation. In principal such initiators are known to the person skilled in the art. Preferred initiators are photoacids such as diaryliodonium salts, triarylsulfonium salts and s-triazines. Further examples are sulphonic acids, like, e.g. para-toluene sulphonic acid, and thermal acids, like, e.g. ammonium nitrate.

Preferred values of the lower limit of the composition are:

- component A: 60 % by weight, most preferably 75 % by weight.
- component B: 2 % by weight, most preferably 5 % by weight.
- component C: 0 % by weight, most preferably 0.5 % by weight.

Preferred values of the upper limit of the composition are:

- component A: 98 % by weight, most preferably 95 % by weight.
- component B: 40 % by weight, most preferably 25 % by weight.
- component C: 5 % by weight, most preferably 2 % by weight.

The above given % by weight values are related to the total weight of the components A, B and C.

Preferably, the polymerizable mixture according to the invention additionally comprises a component D in an amount of from 0.5 to 50000 % by weight related to the total weight of the components A, B and C, wherein D is a solvent or a mixture of two or more solvents, being capable of dissolving the components A, B and C.

In this case the term dissolving means that a solution, emulsion or suspension of the components A, B and C can be produced, optionally with the aid of one or more emulsifiers or surfactants.

The solvents or solvent mixtures are advantageously compatible with solution coating techniques. Preferred solvents are aliphatic or cycloaliphatic ketones, alcohols and ethers, like e.g. cyclohexanone, butanone, iso propyl alcohol (IPA), butanol, ethyl lactate, propylene glycol methyl ether acetate (PGMEA) and propylene glycol methoxy propanol (PGME), as well as mixtures thereof. The solvent or solvent mixture is preferably chosen to stabilize the resulting mixture, which also increases its shelf life.

In addition to component D, the mixture according to the invention may comprise at least one surfactant as a component E to adjust the surface energy of the formulation and the resultant film in order to obtain desired wetting, rheology and adhesion to the substrate and consecutive layers. A further advantage of an added surfactant is a decrease of the water uptake into the resulting amine polymer layer. The surfactant is preferably a non-ionic surfactant, like e.g. polyoxyethylene, polyols, siloxanes, pluoronics and tweens.

Preferred values of the lower limit of the composition are:

- component D: 10 % by weight, most preferably 100 % by weight,
- component E: 0 % by weight, most preferably 0.05 % by weight, and

preferred values of the upper limit of the composition are:

- component D: 10000 % by weight, most preferably 5000 % by weight,
- component E: 2 % by weight, most preferably 0.5 % by weight,

wherein the above given % by weight values are related to the total weight of the components A, B and C.

In another preferred embodiment of the present application, the polymerizable amine mixture according to the invention additionally comprises superfine ceramic particles as a component F.

The superfine ceramic particles F are contained in the polymerizable amine mixture in an amount of from 0 to 80 % by weight, related to the total weight of components A, B and C.

The ceramic particles should be less than 200 nm in average diameter, since that is typically the maximum desired thickness for the insulating layer. Preferably, the particles are less than 100 nm to provide for easy dispersion within the polymeric matrix, and more preferably, about 50 nm in average size.

The particles can be formed from any suitable material which can be formed into particles having a high dielectric, including, for example, high dielectric constant ferroelectric ceramic material including, but not limited to, lead zirconate, barium zirconate, cadmium niobate, barium titanate, and titanates and tantalates of strontium, lead, calcium, magnesium, zinc and neodymium, and solid solutions thereof. By the term ceramic "solid solution" is meant a ceramic system of two or more components in which the ceramic components are miscible in each other. In addition, ceramic materials useful in the invention include barium zirconium titanate (BZT), barium strontium titanate (BST), barium neodymium titanate, lead magnesium niobate, and lead zinc niobate. Each particle can be formed from a single one or a combination of these materials.

The particles included in the layer can all be uniform, or can vary in material composition and/or size. In addition, ceramic materials useful in the invention may be modified by additives including, but not limited to, oxides of zirconium, bismuth, and niobium. Preferably, the ceramic particles comprise barium titanate.

The components of the mixture according to the invention are also chosen to yield good rheology properties, i.e. a viscosity high enough to form a coherent film in a solution coating process and a viscosity low enough to be filterable and spreadable. Preferred viscosity ranges of the mixture are from 300 to 100000 mPa·s.

If in the compounds and components described above and below a substituent, in particular R', R'', R''', R^1, R^2, R^3, R^a, R^b, R^c, R^d is an alkyl group, this may be straight-chain or branched. It is preferably straight-chain, has 1 to 12 carbon atoms and accordingly is preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl or dodecyl. Fluorinated alkyl is preferably C_iF_{2i+1}, wherein i is an integer from 1 to 12, in particular CF_3, C_2F_5, C_3F_7, C_4F_9, C_5F_{11}, C_6F_{13}, C_7F_{15}, C_8F_{17}, C_9F_{19}, $C_{10}F_{21}$, $C_{11}F_{23}$ or $C_{12}F_{25}$.

Cycloalkyl preferably denotes a cyclic aliphatic group containing, e.g., 3 to 7 C atoms such as cyclopropyl, cyclpentyl, and cyclohexyl.

Aryl preferably denotes an aromatic hydrocarbon with 5 to 15 C-atoms, which may be substituted by one or more heteroatoms O, S and/or N, constituting 1, 2 or 3 rings, which may be fused to each other. The most preferred meaning of aryl is phenyl.

Alkylaryl preferbly contains 5 to 15 C atoms in the aryl portion and contains 1 to 12 C atoms in the alkylene portion, for example, benzyl, phenethyl, and phenpropyl.

Halogen is F, Cl, Br or I, preferably F or Cl. In the case of polysubstitution halogen is particularly F.

In the following a process for the manufacture of a dielectric layer of an electronic device according to the invention is described.

In step a) of the process a substrate, which optionally comprises one or more layers or patterns of materials with insulating, semiconductive, conductive, electronic and/or photonic functionalities, is prepared. A number of well-known processing techniques for the manufacture of conventional electronic as well as organic electronic devices, which are preferred according to this invention, are available to a person skilled in the art. For example, the structure of organic electronic devices, the materials and techniques for their manufacture are described in detail in the literature cited in the introduction. The processing is usually done by employing solutions of the organic and/or polymeric materials, like, e.g. by methods described below. The molecules of the resulting film may be aligned in order to achieve anisotropic charge carrier mobility and/or optical dichroism. The organic film is preferably cured, e.g. in defined regions by radiation using a mask. The exposed regions undergo a change in their physical and/or chemical properties, like, e.g. their conductance or solubility. Unexposed regions may be removed due to their higher solubility. By this procedure several layers, which may be patterned, with different electronic functionality may be built on top of each other. Advantageously orthogonal solvents are applied, as described in the introduction, in order not to impair to the previously built layer or pattern. Beside this other patterning methods, like, e.g. microlithography, stamping or micromoulding, may be employed.

In step b) of the process a thin layer of a polymerizable amine mixture comprising one or more amine derivatives as defined in the foregoing is formed onto the substrate or onto defined regions of the substrate. The mixture is preferably applied as a solution, whereby advantageous solvents and their mixtures are described above. Preferably, a polymerizable amine mixture according to the invention is used in step b). Preferred techniques of forming a thin layer allow low cost processing of large areas and/or a high number of substrates. Examples are spin-coating, moulding, like micro-moulding in capillaries, and printing

techniques, like screen-printing, ink-jet printing and microcontact printing. Reel-to-reel fabrication processes are especially preferred. These and other processing techniques are described, e.g. by Z. Bao, Adv. Mater. 2000, 12, 227-230, Z. Bao et al., J. Mater. Chem. 1999, 9, 1895-1904 and the literature cited therein. As mentioned above, the rheology properties of the employed amine derivative mixture can be adjusted in a wide range to meet the requirements of the film forming technique by the choice of the components of the mixture, especially of the substituents of the amine derivative and optionally of the multifunctional component, and of their contents.

In step c) the polymerization of the polymerizable amine mixture of said thin layer is initiated. Depending on the nature of the components of the amine derivative mixture and the optionally employed initiator, the polymerization is initiated for example by rising the temperature, altering the pH, exposing to electromagnetic or particle radiation or to reactive compounds. The polymerization reaction is usually a polycondensation of the amine derivatives and optionally the multifunctional components, whereby for example water or alcohols are set free. The resulting polymer materials may be polymers, copolymers or graft polymers, which are referred to just as polymers in the foregoing and in the following.

The component D or at least a major part of the solvent(s) is removed during and/or after the performance of step c). But, it is also possible to remove solvents while and/or after the polymerizable mixture is formed onto the substrate, before step c) is carried out.

The resulting thin layer of the amine polymer has preferably a thickness of 0.01 to 50 µm, most preferably of 0.1 to 10 µm. The amine polymer material shows preferably a resistivity greater or equal than 10^{+8} Ωcm, more preferably greater or equal than 10^{+10} Ωcm and most preferably greater or equal than 10^{+11} Ωcm. The resulting dielectric constant of the material is preferably greater or equal 4 and most preferably in the range from 4 to 6.

The thin layer may optionally be patterned after the polymerization step. Suitable techniques are known by a person skilled in the art, in particular in the field of microelectronics and microtechnology. Examples of such techniques are etching, lithography, including photo-, UV- and electron-lithography, laser writing, stamping and embossing. Furthermore the layer may also be patterned by polymerizing only defined regions of the polymerizable amine mixture. Polymerization in defined regions may be accomplished for example by using a patterned mask and electromagnetic or particle radiation to initiate the polymerization. The unpolymerized regions of the amine derivative mixture may be removed due to their higher solubility compared to the cured regions.

The formation of the dielectric amine polymer layer may be the last or, usually, an intermediate step in the fabrication of the electronic device. Thus one or more further steps, including steps a) and/or b) and c), may follow the process described above. For example one or more further layers or patterns of materials with insulating, semiconductive, conductive, electronic and/or photonic properties may be applied onto the resulting dielectric layer.

Electronic devices obtainable by the process according to the invention and electronic devices comprising the inventive amine polymer material as a dielectric are also objects of this invention. Preferred devices are microelectronic and/or organic electronic devices and components. Examples are thin film transistors, OFETs, OLEDs, large area driving circuits for displays, in particular LCDs, photovoltaic applications and low-cost memory devices, such as smart cards, electronic luggage tags, ID cards, credit cards and tickets.

The polymer amine material according to the invention is used as a dielectric, including insulator material, in these devices. For example, the polymer amine material is used as a dielectric layer in an OFET between the semiconductive material, being contacted with the source and the drain electrode, and the gate material. Furthermore, the inventive amine polymer material may also be used as an insulator material, to insulate conducting parts of the electronic device. Thus it may be used as a substrate, on top

of which conducting and/or semiconducting materials are deposited, and/or as an insulating material to cover layers or patterns with electronic functionality, thus protecting them from short-circuits or oxidation.

The complete disclosure of all applications, patents and publications mentioned hereinbefore and hereinafter, and cooresponding European patent application No. 02024361.4, filed November 2, 2002, hereby incorporated into this application by way of reference.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Examples

The following examples are set forth to further illustrate the present invention and should not be construed as limiting the spirit or scope of the invention.

1. Polymerizable amine mixtures

The following polymerizable amine mixtures according to this invention are prepared. The content in % by weight is related to the total weight of all components.

1.1 Mixture M1

Component	Compound	Content [%]
A	Melamine-formaldehyde resin, CYMEL 303	39.0
B	None	0
C	p-toluene sulphonic acid	0.9
D	Butan-1-ol butan-2-one	44.5 15.6

1.2 Mixture M2

Component	Compound	Content [%]
A	Melamine-formaldehyde resin, Cymel 1158	35.0
B	None	0
C	p-dodecylbenzene-sulfonic acid	1.5
D	Butan-1-ol butan-2-one	47.0 16.5

1.3 Mixture M3

Component	Compound	Content [%]
A	Melamine-formaldehyde resin, Cymel 1158	35.2
B	None	0
C	p-toluene sulphonic acid	0.6
D	Butan-1-ol butan-2-one	48.2 16.0

1.4 Mixture M4

Component	Compound	Content [%]
A	Melamine-formaldehyde resin, UI20-E	35.0
B	None	0
C	p-toluene sulphonic acid	0.6
D	Butan-1-ol butan-2-one	48.4 16.0

1.5 Mixture M5

Component	Compound	Content [%]
A	Melamine-formaldehyde resin, Cymel 327	35.0
B	None	0
C	p-toluene sulphonic acid	0.6
D	Butan-1-ol butan-2-one	48.4 16.0

The mixtures M1 to M5, which are stable and homogeneous over the time, show a low to medium viscosity. Their rheology properties are very good for applying coating techniques, like for example the coating of surfaces like glass or polyhexylthiophene, which is an organic semiconductor.

2. Preparation of amine polymer materials

Based on the polymerizable amine mixtures M1 to M5 amine polymer materials are prepared. A sample of a mixture is put onto a flat glass substrate which then is spread over the substrate by spin-coating (increasing from 0 to 2000 rpm over a period of 2 seconds and then held at 2000 rpm for 1 minute). The polymerization and crosslinking is performed by heating the substrate at 100°C for a duration of 1 hour in an air atmosphere. The resulting amine polymer layer has a thickness of about 1 micron.

Using the polymerizable mixtures M1 to M5 as defined in the foregoing, amine polymer layers are prepared according to the procedure described above. The surfaces of all polymer layers are very flat, hard, but not brittle and exhibit an excellent cohesion. There is no evidence of pin-hole formation. The following further results are obtained, whereby the lowest resistivity values obtained are given in each case.

Polymerizable mixture	Dielectric Const.	Solvent exposure test	Resistivity [Ωcm]
M 1	4.5	Excellent	$1.5 \times 10^{+14}$
M 2	3.8	Excellent	$3.0 \times 10^{+14}$
M 3	4.5	Excellent	$2.3 \times 10^{+14}$
M 4	4.0	100.44%	$7.5 \times 10^{+12}$
M 5	5.2	Excellent	$8.0 \times 10^{+13}$

The solvent exposure test is performed by cutting a trench approximately 100 μm wide into the amine polymer layer and measuring the depth of the trench. Then dichloromethane is applied onto the trench and leaving it immersed for 15 minutes. The extent to which the film is affected by the solvent is then measured by changes in the trench profile (swelling or dissolving). If there is no measurable change then the film is said to have excellent resistance, otherwise a percentage change is given where a positive value signifies swelling.

As it can be seen from the results above, in particular the mechanical and electrical properties as well as the solvent resistance, the amine polymer materials according to the present invention are particularly well suited as dielectric layers of electronic devices.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.